

METHOD FOR GROWING GROUP-III NITRIDE SEMICONDUCTOR HETEROSTRUCTURE ON SILICON SUBSTRATE

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BACKGROUND OF THE INVENTION

1. Field of the Invention

10 The present invention generally relates to a semiconductor structure, and more particularly to a method for growing a group-III nitride semiconductor heteroepitaxial structure on a silicon substrate.

2. Description of the Prior Art

15 The structure of semiconductor light-emitting diode (LED) comprises a substrate, a light emitting structure, and a pair of electrode for powering the diode. The substrate can be opaque or transparent. Light emitting diodes that are based on gallium nitride compounds generally comprise: a transparent, insulating substrate, e.g., a sapphire substrate. To overcome the difficulty of the substantial lattice mismatch between an insulating substrate, e.g., a sapphire substrate, and GaN compound semiconductor, it is a common practice to provide a thin buffer layer or nucleation layer on the sapphire substrate, which is followed by a layer on which an LED structure is grown. Growth of 20 single crystals on insulating substrates has been studied for many years. Early works included growth of both silicon and III-V compound semiconductors on a variety of insulating substrates including sapphire. In these studies it was determined that use of nucleation or buffer layers 25

reduces the occurrence of imperfections and the tendency towards twinning in the thicker layer grown thereon.

Group III nitride semiconductors [GaN (gallium nitride), InN (indium nitride), AlN (aluminum nitride), and their alloys] have become the materials of choice for many optoelectronic applications, especially in the areas of fully-color or white-light light emitting diodes (LEDs) and blue laser diodes (LDs). Some scientists and engineers have even predicated that group-III nitrides will become all-around semiconductors besides their already-commercialized applications in optoelectronics. At present, the major barrier for widespread applications of nitrides is the lack of perfectly lattice-matched substrates for epitaxial growth. Sapphire (Al_2O_3) and silicon carbide (SiC) are two most popular choices as growth substrates. But, besides the large lattice mismatch, the insulating nature of sapphire renders the processing of nitride devices more difficult and costly. On the other hand, the high price and limited size of silicon carbide also make the widespread GaN-on-SiC applications difficult. GaN-on-Si epitaxial technology represents an interesting alternative, which can eventually integrate the existing Si-based microelectronic technology and the novel functionalities provided by the group-III nitrides.

For GaN-on-Si heteroepitaxy, the AlN buffer layer approach yields the best results reported in the literature, leading to the demonstration of light-emitting diodes on Si. However, the mutual solubility of Al and Si is very high at the AlN buffer-layer growth temperature (about 820°C vs. eutectic temperature 577°C). Therefore, the inter-diffusion of Al and Si at the interface is severe, resulting in high unintentional doping levels

in the epilayer and the Si substrate as well as the degradation in the film structural and optical quality.

On the other hand, It has been found that an amorphous or 5 polycrystalline SiN_x [silicon nitride (Si_3N_4) or silicon subnitride] layer can be formed by intentional or unintentional nitridation of the silicon substrate surface during the first stage of the group-III nitride growth. Moreover, Si_3N_4 is known to be an effective diffusion barrier material. However, this amorphous or polycrystalline SiN_x layer is prone to cause 10 detrimental effects on the properties of grown GaN films on the Si substrate since it is not possible to grow a high-quality crystalline film on a amorphous or polycrystalline surface. Therefore, it has been a common practice in the growth of group-III-nitrides film on the silicon substrate to avoid the formation of an amorphous or polycrystalline SiN_x 15 layer during the first stage of the group-III nitride growth. To overcome the effects of amorphous or polycrystalline SiN_x on the growth quality and to facilitate an effective diffusion barrier layer, formation of a single-crystal diffusion barrier layer which can be lattice matched to the Si(111) surface is highly desirable.

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SUMMARY OF THE INVENTION

It is an object of this invention to provide a multiple-layer buffer, comprising at least two layers of distinct material with sharp material 25 transitions and epitaxial alignments between the layers on the crystalline silicon substrate and between the bottom layer of the buffer with the crystalline silicon substrate, to resolve the issue of the inter-diffusion between the interfaces of AlN/Si , GaN/Si , or InN/Si .

5 It is a further object of this invention to provide a single-crystal AlN/Si₃N₄ double buffer layer with coincident lattice conditions on a Si(111) substrate that can alleviate the problems of lattice mismatch and

interdiffusion, thereafter inducing high-quality heteroepitaxial growth.

According to abovementioned objects, the present invention provides a structure for resolving the issue of auto-doping, resulting from Al/Si, Ga/Si, or InN inter-diffusion when grown with a group-III

10 nitride buffer layer. The structure comprises a Si(111) substrate that surface has been reconstructed by *in-situ* thermal annealing to remove the remained thin oxide layer and to prepare clean and smooth silicon surface at high temperature. Then, the key feature of the present invention, a multiple-layer buffer layer is formed on the reconstructed

15 Si(111) substrate. The multiple-layer buffer includes a single-crystal silicon nitride layer and a single-crystal AlN layer or other group-III nitride semiconductor epitaxial layer thereon. Next, the GaN epilayer is grown on the multiple-layer buffer. The advantage of the present invention is that the multiple-layer buffer mechanism can improve

20 heteroepitaxial growth with large lattice mismatch. Furthermore, the 1:2 and 5:2 coincident lattices formed at the interface of the single-crystal silicon nitride (Si₃N₄)/Si(111) and the interface of the single-crystal AlN(0001)/single-crystal silicon nitride (Si₃N₄) respectively can be used to facilitate the multiple-layer buffer for high-quality GaN-on-Si 25 heteroepitaxial growth. Thus, the inter-diffusion between group-III elements (Al, In, or Ga) and Si can be resolved and the epitaxial growth quality can be improved.

Moreover, the present invention provides a method for forming a group-III heteroepitaxial structure on a Si(111) substrate. The key feature of the present invention is that the multiple-layer buffer is formed on the Si(111) substrate. The multiple-layer buffer comprises a 5 single-crystal silicon nitride (Si_3N_4) layer that is formed on the Si(111) substrate by introducing reactive nitrogen-plasma to the reconstructed Si(111) surface in the controlled manner to prevent the formation of amorphous or polycrystalline SiN_x layer. Then, another buffer layer is an AlN layer or other group-III nitride layer, which is grown epitaxially on 10 the single-crystal silicon nitride layer. Similarly, the group-III nitride heteroepitaxial structure is epitaxially grown on the AlN layer.

BRIEF DESCRIPTION OF THE DRAWINGS

15 The foregoing aspects and many of the attendant advantages of this invention will become more readily appreciated as the same becomes better understood by reference to the following detailed description, when taken in conjunction with the accompanying drawings, wherein:

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FIG. 1 is a flow diagram showing the steps for growing a group-III nitride semiconductor heteroepitaxial structure on a Si(111) substrate in accordance with a method disclosed herein;

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FIG. 2A through FIG. 2D are schematic representations the structure of various stages during the formation of a group-III nitride semiconductor heteroepitaxial structure on a Si(111) substrate in accordance with a method disclosed herein;

5 FIG. 3 is a schematic representation the SIMS depth profiles nears the buffer/substrate and the epilayer/buffer interface regions for samples with a single-crystal AlN/Si₃N₄ double buffer layer (a) and a single-crystal AlN single buffer layer (b) in accordance with a method disclosed herein;

10 FIG. 4A is a schematic representation the low-temperature PL spectra of GaN epilayer grown on Si(111) using single-crystal AlN/Si₃N₄ and AlN buffer layers in accordance with a structure disclosed herein;

15 FIG. 4B is a schematic representation showing the Arrhenius plots of the luminescence intensities of free exciton (FX) grown on a single-crystal AlN/Si₃N₄ double buffer layer and neutral-donor-bound exciton grown on single-crystal AlN single buffer layer in accordance with a structure disclosed herein; and

20 FIG. 5 is a schematic representation showing the room temperature Raman spectra taken from the GaN epilayer grown on Si(111) substrate using single-crystal AlN/Si₃N₄ and AlN buffer layers in accordance with a structure disclosed herein.

DESCRIPTION OF THE PREFERRED EMBODIMENT

25 Some sample embodiments of the invention will now be described in greater detail. Nevertheless, it should be recognized that the present invention can be practiced in a wide range of other embodiments besides those explicitly described, and the scope of the present invention is

expressly not limited except as specified in the accompanying claims.

According to the present invention is to provide a method and a stacked buffer structure for improving the inter-diffusion issue that
5 occurs between AlN/Si, GaN/Si, and InN.

Group-III nitrides on silicon heteroepitaxy have recently demonstrated to be a viable alternative for growing high-quality group-III nitride films for optoelectronic, electronic, and surface acoustic wave
10 device applications. Besides the availability of larger size (up to 12 inch in diameter), low cost, and excellent crystal quality of Si substrates, Si also possesses excellent material properties such as doping properties (amphoteric type and high carrier concentration), cleavability, good thermal conductivity (about 3 times larger than that of sapphire), and
15 mature processing techniques. These advantages of Si substrates can open up many novel applications of group-III nitride materials, including the potential integration of GaN and Si technologies. The reason that high-quality GaN-on-Si heteroepitaxy is feasible that is due to the possible lattice matching of hexagonal wurtzite epitaxial films and
20 diamond Si(111) crystal faces.

The stacked buffer layer consists of constituent layers, which can form coincident lattices at layer/layer and layer/substrate interfaces. In the preferred embodiment of the present invention, the buffer layer comprising at least two layers of distinct material with sharp material
25 transitions and epitaxial alignments between the layers and between the bottom layer of the buffer layer and the Si(111) substrate. For the case of GaN-on-Si(111) heteroepitaxy, the present invention utilizes the 1:2 and

5:2 coincident lattices formed at the β -Si₃N₄ (0001)/Si(111) and AlN (0001)/ β -Si₃N₄(0001) interfaces respectively to facilitate the double buffer layers for high-quality GaN-on-Si heteroepitaxial growth. By using this buffer technique, the present invention can resolve the issue 5 of auto-doping, resulting from Al/Si inter-diffusion when grown with a single AlN (0001) coincident buffer. As the result, the epitaxial quality of GaN film is also significantly improved.

10 GaN on Si(111) heteroepitaxy constitutes a large +20.4% in-plane lattice mismatch ($\equiv (a_{\text{Si}} - a_{\text{GaN}}) / a_{\text{GaN}}$; $a_{\text{GaN}(0001)}=3.189\text{\AA}$; $a_{\text{Si}(111)}=3.840\text{\AA}$) and large thermal expansion mismatch. Fortunately, by using a buffer layer with coincident lattice conditions can alleviate the lattice mismatch. For example, a 5:4 lattice coincidence between AlN (0001) ($a_{\text{AlN}(0001)}=3.112\text{\AA}$) and Si(111) can reduce the lattice mismatch from 15 23.4% (tensile strain) to an effective lattice mismatch of -1.3% (compressive strain). As a result, two-dimensional smooth epitaxial growth mode was found to be possible due to the reduced strain.

20 The growth processes were conducted in a molecular-beam epitaxy (MBE) apparatus equipped with a radio frequency (RF) nitrogen plasma source. The base pressure in the MBE growth chamber was about $6*10^{-11}$ Torr. High-purity Ga and Al metals were used for the conventional effusion cells. Nitrogen gas (N₂) was purified through a nitrogen purifier before fed into the radio-frequency (rf) plasma source. 25 Nitrogen plasma was generated under the same conditions during all the growth processes. The RF power is about 450 watt and the nitrogen flow rate of the nitrogen is about 0.5 sccm. Three-inch Si(111) substrate (boron-doped p-type) was chemical etched before loading into

the MBE chamber. The Si(111) substrate was further thermally annealed *in situ* to remove the remained thin oxide layer and to prepare a clean and smooth silicon surface at high temperature. The Si(111) substrate prepared by this process showed a clear (7*7) surface reconstruction, confirmed by the reflection high-energy electron diffraction (RHEED) pattern at about 800°C.

Furthermore, the RHEED pattern indicates a high-quality and smooth reconstructed Si surface prior to the growth process. The 10 substrate temperature was calibrated by observing the (7*7) to (1*1) phase transition of Si(111) surface at 875°C. In the present invention, two different buffer-layer systems for GaN growth on Si (111) substrates were prepared for comparison. Both samples consist of an AlN buffer layer with a thickness of 30 nm. The only difference is that one sample 15 contains a single-crystal β -Si₃N₄ layer [1.5 nm-thick layer with an abrupt interface with the Si(111) substrate, as confirmed by transmission electron microscopy (TEM)] before the AlN layer growth. Single-crystal silicon nitride layer can be formed by nitridation of the Si(111) surface under the reactive nitrogen plasma for 30 sec at a 20 substrate temperature of about 900°C. The 30 nm thick AlN buffer layers were grown epitaxially at 820°C with a growth rate of 0.12 um/hr. Furthermore, the 240-nm-thick GaN epitaxial layers were grown on the buffer layers at a lower substrate temperature (720°C) with a growth rate of 0.08 um/hr. After the MBE growth, the grown GaN surface (cooling 25 to 500 to 600 °C) showed a (2*2)-reconstruction pattern under the nitrogen flux, indicating a Ga-polar film. The Ga-polar GaN film is known to have better structural and optic properties

FIG. 1 shows a flow chart of the method for forming a double buffer layer on the Si(111) substrate, wherein, FIG. 1 divided into FIG. 1A and FIG. 1B to show the formation process of double buffer layer on the Si(111) substrate. Step 1 illustrates the Si(111) substrate that were 5 thermally annealed *in situ* to remove the remained thin oxide layer and to prepare a clean and smooth silicon surface at high temperature. The Si(111) substrate prepared by the process showed a clear (7*7) surface reconstruction, that can be confirmed by the RHEED pattern at about 800°C. Step 2 illustrates the reactive nitrogen-plasma is introduced to 10 the surface of the reconstructed Si (111) substrate in a controlled manner to form the single-crystal silicon nitride (Si_3N_4) diffusion-barrier buffer layer by nitridation of the surface of the Si (111) substrate. The surface of single-crystal Si_3N_4 diffusion-barrier buffer layer formed in step 2 is terminated by nitrogen surface adatoms. Step 3 illustrates the 15 process for forming Al pre-deposition atomic layer on the single-crystal nitrogen-terminated Si_3N_4 diffusion-barrier buffer layer. Then, a thermal annealing process is performed to the Al pre-deposition atomic layer to form an AlN monolayer on the single-crystal Si_3N_4 diffusion-barrier buffer layer without the reactive nitrogen species (step 20 4). Next, an epitaxial AlN buffer layer is formed on the single-crystal Si_3N_4 diffusion-barrier buffer layer by performing an AlN epitaxial growth process on the AlN monolayer (step 5). Finally, the GaN film with a Ga-polarized surface or a group-III nitride semiconductor 25 heteroepitaxial structure is grown by an epitaxial growth method on the single-crystal AlN buffer layer (step 6).

Then, referring to FIG. 2A, the Si(111) substrate 10 is initially treated by *in-situ* annealing process or *ex-situ* wet etching process (such

as etching by an HF solution) to remove the remained thin oxide layer and to prepare a clean and smooth silicon surface. The Si(111) substrate 10 prepared by the thermal annealing process shows a clear (7*7) surface reconstruction, and is confirmed by the reflection 5 high-energy electron diffraction (RHEED) pattern at about 800°C. The RHEED pattern can be used to indicate a high-quality and smooth reconstructed Si(111) substrate surface prior to the growth processes. The substrate temperature is calibrated by observing the (7*7) to (1*1) phase transition of Si(111) surface at 875°C.

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Next, the key feature of the present invention is that the diffusion-barrier buffer layer 12 such as a single-crystal silicon nitride layer is formed by nitrogen-plasma nitridation of the surface of Si(111) substrate 10. The nitridation process is performed by exposing the 15 surface of Si(111) substrate 10 to the reactive nitrogen plasma for about 30 seconds at a substrate temperature of about 900°C. Exposure time is critically controlled to prevent the unwanted formation of amorphous or polycrystalline SiN_x layer. In the present invention, the single-crystal silicon nitride [β -Si₃N₄(0001)] layer 12 can also be formed on the Si(111) 20 substrate 10 by introduction of reactive nitrogen-containing species including NH₃ while the surface of Si (111) substrate 10 held slightly higher than the (7*7) to (1*1) phase transition temperature. A single-crystal (4*4) surface-reconstruction (alternatively, the 25 "(8*8)"-reconstruction in terms of the Si (111) substrate 10 lattice parameter) usually forms after such controlled nitridation process.

The RHEED pattern shows the "(8*8)"-reconstructed surface after introducing the reactive nitrogen plasma to the surface of Si(111)

substrate at the substrate temperature of 900°C for about 30 seconds. The RHEED pattern shows that are two different ordering on β -Si₃N₄(0001). One ordering corresponding to the topmost "(8/3*8/3)"-ordered nitrogen adatoms and the other corresponds to the 5 "(8*8)" lattice periodicity. In the previous scanning tunneling microscopy experiments, the "(8*8)" ordering was confirmed to be the reconstruction unit cell of the β -Si₃N₄(0001) surface.

Then, the growth of AlN buffer layer 16 in the double buffer layer 10 system was started on the nitrogen-terminated Si₃N₄ reconstruction surface as shown in FIGS. 2B and 2C. After 15 seconds of Al pre-deposition process, the Al atomic layer 14 is formed on the surface of single-crystal Si₃N₄ layer 12. Then, a single-crystal AlN buffer layer 16 stacked on the single-crystal Si₃N₄ layer 12 is formed first by performing 15 a thermal annealing process to the AlN pre-deposition atomic layer 14. The AlN (0001)-(1*1) ordering appears in the streaky RHEED pattern after the thermal annealing step. The RHEED pattern indicates that Al atoms are bounded with the topmost N adatoms of the single-crystal Si₃N₄ layer 12 and the surface is very smooth. It should be noted that 20 the reciprocal space periodicities along the bulk β -Si₃N₄(0-110) 12 and AlN(0-110) 16 directions are 4:5 and this condition can be confirmed in the RHEED pattern. Then, an AlN buffer layer 16 is grown by an epitaxial growth method on the single-crystal Si₃N₄ layer 12. In addition, it is also possible that the second buffer layer stacked on the 25 single-crystal Si₃N₄ diffusion-barrier buffer layer 12 is a GaN layer or InN (indium nitride) layer.

In order to compare the effects of single-crystal AlN single

buffer and AlN/Si₃N₄ double buffer layer on the grown film quality, the AlN buffer layer 16 with an identical thickness about 30 nm were grown epitaxially on two Si substrates with and without the single-crystal Si₃N₄ layer 12 at a substrate temperature of 820°C with a growth rate of 0.12
5 um/hr, as shown in FIG. 2D. Moreover, the GaN epitaxial layers 20 with an identical thickness about 240 nm were grown on the single-crystal AlN buffer layers 16 of these two samples at a lower substrate temperature which is about 720°C with a growth rate of 0.08 um/hr. After the MBE growth, the grown GaN surface after cooling to 500 to 600
10 °C shows a (2*2)-reconstruction pattern under the nitrogen plasma flux.

As referring to FIG. 2D, the present invention provides a light-emitting device structure with a double buffer layer to resolve the issue of the auto-doping, resulted from the inter-diffusion of Al/Si and
15 Ga/Si when grown with a single AlN(0001) coincident buffer. The light-emitting device provides a Si(111) substrate 10 with in-plane lattice constant of 3.84 angstroms. The key feature of the present invention is a double buffer layer on the Si(111) substrate 10. In the preferred embodiment of the present invention, the double buffer layer can
20 improve the light-emitting efficiency for the light emitting device, wherein the double buffer layer includes a single crystal silicon nitride layer (Si₃N₄) (0001) 12 with in-plane lattice constant 7.61 angstroms, and the AlN(00001) layer 16 with in-plane lattice constant 3.112 angstroms.

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In addition, the present invention shows a streaky RHEED pattern after 10-min AlN growth at 840°C and indicates that the resulting epitaxial AlN buffer layer 16 has a smooth surface and is of

high film quality. A GaN epilayer grown on the single-crystal $\text{Si}_3\text{N}_4/\text{AlN}$ double buffer layer by MBE also has a smooth surface morphology and high crystalline quality as demonstrated by the *in-situ* streaky RHEED pattern and is confirmed by *ex-situ* X-ray diffraction (XRD) and atomic force microscopy (AFM) measurements. Herein, the possible overgrown heteroepitaxial structure on top of the double buffer layer includes a group-III nitride semiconductor single epitaxial layer or group-III nitride semiconductor heteroepitaxial multiple-layer. From the *in-situ* RHEED and *ex-situ* XRD measurements, the present invention can determine that 1:2 and 5:2 coincident lattice interfaces are formed at β - $\text{Si}_3\text{N}_4(0001)/\text{Si}(111)$ and $\text{AlN}(0001)/\beta$ - $\text{Si}_3\text{N}_4(0001)$ interfaces, respectively.

Furthermore, the following epitaxial orientation relationships are found by the RHEED and XRD studies: β - $\text{Si}_3\text{N}_4(0001) \parallel \text{Si}(111)$; β - $\text{Si}_3\text{N}_4[0\bar{1}10] \parallel \text{Si}[11\bar{2}]$; β - $\text{Si}_3\text{N}_4[2\bar{1}\bar{1}0] \parallel \text{Si}[\bar{1}10]$ and $\text{AlN}(0001) \parallel \beta$ - $\text{Si}_3\text{N}_4(0001)$; $\text{AlN}[0\bar{1}10] \parallel \beta$ - $\text{Si}_3\text{N}_4[0\bar{1}10]$; $\text{AlN}[2\bar{1}\bar{1}0] \parallel \beta$ - $\text{Si}_3\text{N}_4[2\bar{1}\bar{1}0]$. Thus, the GaN/AlN/ β - Si_3N_4 c-axis is perpendicular to the surface of $\text{Si}(111)$ substrate. It is tempting to perform heteroepitaxy of GaN on the $\text{Si}(111)$ substrate using a single β - Si_3N_4 buffer layer (without the AlN buffer layer). However, the present invention confirms that the resulting growth is rough and polycrystalline in the first growth stage as indicated by the spotty RHEED pattern during the initial GaN film growth. Therefore, the double buffer layer approach can yield better interface properties between epilayer and buffer layer.

The GaN epilayer grown under the same growth conditions using a single AlN buffer layer also shows a similar high-quality RHEED pattern.

Therefore, in order to compare the influences of these different buffer layers, secondary-ion mass spectroscopy (SIMS), XRD, photoluminescence (PL), and Raman scattering measurements were conducted to compare the structural and the optical properties of these 5 GaN films with and without the single-crystal β -Si₃N₄ buffer layer.

Firstly, the impurity distribution in the growth direction can be detected by SIMS. In order to investigate the auto-doping effects while GaN grown on the Si(111) substrate, the present invention focus on Al 10 and Si ion signal depth profiles in the GaN/AlN and AlN/Si interface regions. The SIMS spectra were obtained by using a 7.7 keV Cs⁺ primary beam and were used to probe Al and Si depth profiles in GaN films grown on Si(111) substrate using two buffer layer systems. The depth zero points of each SIMS spectrum are set at the top of Si(111) 15 substrates. Focus on the Si depth profiles in AlN buffers and GaN epitaxial layers, the magnitudes of the Si ion signal are indicated by the solid arrows in FIG. 3. From the SIMS spectra, the magnitudes of Si impurities in the AlN buffer layer and the GaN film using a single-crystal β -Si₃N₄(0001)/AlN(0001)/Si(111) double buffer layer is about one order 20 of magnitude lower than that using an AlN single buffer layer.

Not only the single-crystal Si₃N₄ layer inhibits the Si diffusion into the AlN and GaN layers, it also prevents the Al diffusion into the silicon substrate during the high temperature growth of AlN buffer layer. And, 25 the magnitude of the Al ion signal in Si(111) substrate is also about one order of magnitude lower than that grown without the single-crystal silicon nitride diffusion barrier layer. Therefore, the SIMS spectra show that single-crystal Si₃N₄ layer inhibits Si diffusion into the AlN and GaN

layer and Al diffusion into the silicon substrate effectively during the AlN high-temperature growth and the sequential GaN epitaxial growth stage.

FIGS. 4A and 4B show the comparison of the optical properties of 5 GaN films that grown on different buffer layers. The low-temperature (6.7 K) PL spectra indicate that the GaN film grown on single-crystal AlN/Si₃N₄/Si(111) has a smaller full width at half maximum (FWHM) of neutral-donor-bound exciton (D^oX) near-band-edge luminescence peak than that of film grown on AlN(0001)/Si(111). The decrease in the 10 FWHM value of PL peak (12 meV vs. 20 meV) is consistent with the deduction of dislocation density ($7 \times 10^8 \text{ cm}^{-2}$ vs. $1.1 \times 10^9 \text{ cm}^{-2}$) measured by AFM, confirming a significant improvement in the epilayer crystalline quality. The inset in FIG. 4A displays the main luminescence peak position in the PL spectra of GaN grown on single-crystal 15 AlN/Si₃N₄/Si(111) at different temperatures, indicating that the dominant PL peak changes to the free exciton (FX) emission at increasing temperatures (higher than 70 K, $70 k_B T \approx$ the localization energy E_{loc} of neutral Si donor). In contrast to this behavior, for the AlN single-buffer layer sample, the D^oX peak can be followed up to the room 20 temperature. This observation is consistent with the SIMS results; i.e., the GaN film grown on the single-crystal AlN/Si₃N₄/Si(111) contains much less Si impurities.

FIG. 4B presents the Arrhenius plots of the luminescence 25 intensities of FX in GaN grown on the single-crystal double buffer layer and D^oX in GaN grown on the single buffer layer. From the Arrhenius plots, the activation energy of FX (E_x) in the GaN grown on the single-crystal AlN/Si₃N₄/Si(111) was obtained by fitting the thermal

activation relation is about 25 meV, in good agreement with the reported value for FX in undoped GaN. Furthermore, the activation energies of the non-radiative recombination of D^oX in GaN grown on the single-crystal AlN/Si₃N₄/Si(111) can be fitted by using two thermal 5 activation energies (E_{a1} and E_{a2}). The obtained values of E_{a1} and E_{a2} correspond well to the known localization energy ($E_{loc}\sim 6$ meV) and donor binding energy ($E_D\sim 29$ meV) of Si impurities in GaN.

10 The present invention performed Raman scattering measurements to compare the crystal qualities of GaN epitaxial layers grown on Si (111) by using different buffer layer systems. FIG. 5 displays typical non-polarized Raman spectra in logarithmic intensity scale collected in backscattering geometry along the GaN c ([0001]) axis (along the growth direction) using the 514.5 nm radiation of an Ar⁺ ion 15 laser as a light source, including the dominant phonon peak from Si substrate near 520 cm⁻¹. The phonon bands near 568 cm⁻¹ in each Raman spectrum that are GaN E₂ bands. Besides, the A₁ (LO) band near 735 cm⁻¹ is observed only in the GaN film grown on the single-crystal double buffer layer and it represents that this GaN film 20 has a lower carrier concentration. According to the previous investigation, the ratio of A₁ (LO) to E₂ Raman intensity is ~3 for the undoped GaN films. The present invention measures the A₁(LO) to E₂ intensity ratio of the GaN film grown on the single-crystal double buffer layer is about 3.3 (only slightly larger than 3), indicating the carrier 25 concentration is nearly as low as an undoped GaN film. This is consistent with the SIMS spectra, which show a lower Si concentration in the GaN film grown on Si(111) using a single-crystal AlN/Si₃N₄ double buffer layer.

Although specific embodiments have been illustrated and described, it will be obvious to those skilled in the art that various modifications may be made without departing from what is intended to
5 be limited solely by the appended claims.